

V₂O₃(0001) on Au(111) and W(110): Metal to Insulator Transition Induced by Surface Termination

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Thin films of V₂O₃ have been grown on Au(111) and W(110). It is possible to prepare two different surface terminations: the first one is vanadium terminated whereas the second one exhibits additional oxygen atoms, forming vanadyl groups with the surface vanadium atoms. The electronic structure was studied for both terminations by photoelectron spectroscopy. While the first surface is metallic at room temperature like V₂O₃ bulk, the second surface with the vanadyl groups shows a gap at the Fermi level.

INTRODUCTION

Band theory's prediction whether a material at 0K is metallic or insulator is based on the filling of electronic bands: For insulators, the highest filled band is completely filled ; for metals, it is partially filled. This band picture is based on noninteracting or weakly interacting electron systems. However, many transition metal oxides with a partially d electrons band show insulator behavior. The breakdown of the band theory for these compounds evidences the importance of electron-electron correlations. V₂O₃, with its very rich phase diagram, is a good example to demonstrate the complexity of transition metal oxides. Of particular interest is its paramagnetic metallic (PM) to antiferromagnetic insulator (AFI) phase transition at 150 K. This metal insulator transition (MIT) is generally believed to result from electron-electron correlations(Mott-Hubbard transition). However, despite the large number of experimental and theoretical works done on V₂O₃, the understanding of the transition and the nature of the ground state are still controversial.

Most of the experimental studies on V₂O₃ reported in the literature were done on single crystals or powder materials and only a few on thin or ultra thin films. We are able to grow a thin V₂O₃ film which exhibits the same geometric and electronic structure as a single crystal. We showed that two terminations for the V₂O₃(0001) surface exist [1]. The difference between both surface terminations is the presence or absence of additional oxygen atoms at the surface. These oxygen atoms form a double bond with the surface vanadium atoms, thus creating vanadyl groups. We observed a dramatic dependence of the electronic structure on the surface termination. Indeed, our photoemission results evidence a MIT induced by the formation of the vanadyl species at the surface.

EXPERIMENTAL

Three different UHV systems were employed for this work. Angle resolved UV photoelectron spectra (ARUPS) were taken in the first one using a VSW ARIES spectrometer with a rotatable electron analyzer and a Specs helium discharge lamp as source for UV radiation. X-ray photoemission spectroscopy (XPS) and near edge X-ray absorption spectroscopy (NEXAFS) measurements were performed in the second system at the BESSY II synchrotron radiation source in Berlin. Infrared absorption spectra (IRAS) were taken in the third system with a modified Mattson RS-1 FTIR spectrometer. The measurement temperature was 300 K for all the spectra shown here.

Au(111) substrate was cleaned in UHV by alternating cycles of Argon sputtering and annealing at 1150 K. To remove carbon from W(110) we repeated the usual cleaning cycle consisting of heating the sample first to 1800 K in 10⁻⁶ mbar of oxygen during a few minutes and then to 2300 K without oxygen. The V₂O₃(0001) film was prepared for both substrates by evaporation of metallic vanadium in an oxygen atmosphere (10⁻⁷ mbar), followed by annealing at 700 K in 5.10⁻⁸ mbar of oxygen. The vanadium oxide so obtained is stable under UHV conditions (10⁻¹⁰ mbar) up to high temperatures (at least 1050 K). However, heating to higher temperatures than 800 K leads to diffusion of gold substrate atoms towards the surface. This diffusion phenomenon does not seem to occur with the tungsten substrate.

RESULTS

V₂O₃ has corundum structure like Al₂O₃, i.e. the oxygen atoms form a hexagonal lattice and two third of its octahedral sites are occupied by vanadium atoms. The good quality of the LEED pattern obtained for a 30 Å thick film on both substrates provides evidence for satisfactory epitaxial growth. We controlled the stoichiometry of the V₂O₃ film with XPS and NEXAFS. We can conclude that the film we obtained is identical in terms of its stoichiometry and electronic structure to a single

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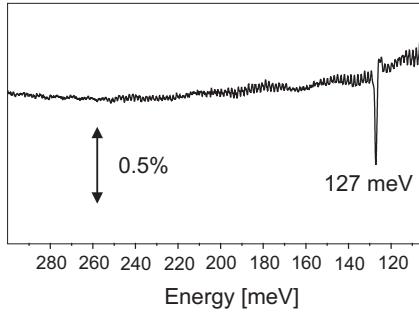


FIG. 1: IRAS: spectrum for $-V=O$ termination divided by spectrum for $-V$ termination. The absorption peak corresponds to the V-O stretching vibration of the vanadyl groups

crystal of V_2O_3 (see [1] for details about the growth of the thin film).

The first surface termination was obtained immediately after the normal preparation process described above. The second one was obtained from the first one by heating the sample up to 600 K with electron bombardment for a short time (few seconds). Note that this process is reversible : annealing the second surface leads to the first one again. We performed IRAS measurements for both terminations. A commonly used method by IRAS in surface science is to take a first spectrum for a reference surface and a second one for the surface to analyze and then make the ratio between both sets of data. By adsorption experiments, for example, the reference surface is the clean surface and the surface to analyze the covered surface. It allows one to observe the absorption features of only the adsorbate. We used this method here, setting the data of the second terminated surface as reference to analyze the data of the first surface. The result, shown in Figure 1, exhibits only one absorption feature at 127 meV ($=1023\text{ cm}^{-1}$).

A feature at the same energy was previously observed for $V_2O_5(001)$ by high resolution electron energy lost spectroscopy (HREELS) and assigned to the V-O stretching vibration of vanadyl groups ($V=O$) [2]. Netzer et al. showed also the existence of vanadyl groups in $V_2O_3(0001)/Pd(111)$ [3]. We therefore conclude that the difference between both surface terminations is only the presence of vanadyl species on the first surface. In the following we will call the first surface termination with the vanadyl species the $-V=O$ termination and the other one, where the $V=O$ groups have been removed, the $-V$ termination.

We used UPS to study the surface electronic structure of the V_2O_3 film with both $-V$ and $-V=O$ terminations. We observe mainly four differences between the spectra of the $-V=O$ termination and the spectra of the $-V$ termination, as will be discussed in detail below. First, there is an increase of the work function. Second, the O 2p band exhibits a shift towards lower binding energies. Third, the spectra exhibit additional features within the O 2p

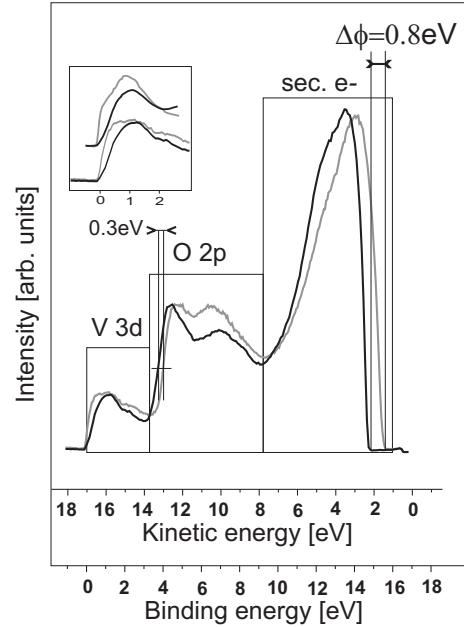


FIG. 2: UPS (HeI) on $V_2O_3(0001)/Au(111)$ for the $-V$ (grey) and $-V=O$ (black) terminations at normal emission. The difference of the low energy cutoff corresponds to the difference of the work function between the two terminations. Inset : comparison of our spectra (below) with spectra from [4] of V_2O_3 single crystal above and below the transition temperature (above) in the V 3d emission region

band. And at last, the spectra show a decrease of emission at the Fermi energy. We show in Figure 2 a He I spectrum for each termination at room temperature. The light angle of incidence was 45° with respect to the surface normal; the electrons were detected in the direction normal to the surface. One can distinguish three bands of emission. The first and least intense one between the binding energies (E_B) 0 (corresponding to the Fermi energy E_F) and 3.5eV originates from the V 3d bands. The second in the middle from about 3.5 to 9.5eV corresponds to the O 2p band. The last one arises from secondary electrons. The assignment for the first two features corresponds to an interpretation in terms of a simple ionic picture but band structure calculations [5, 6, 7] and theoretical analysis of core level spectra [8] show evidence for a strong V 3d - O 2p hybridization. The low energy cutoff gives us information about the work function of the material. We find a difference of 0.8 eV between the two terminations. This is not surprising since the vanadyl species form a dipole with its negative end outwards, which increases the work function. The O 2p band of the $-V=O$ terminated surface exhibits a shift of about 0.3 eV towards lower binding energies relative to the $-V$ terminated surface. This shift is indicated on Figure 2.

We investigated more thoroughly the differences in the electronic structure between both surfaces using HeII angle resolved photoelectron spectroscopy. We performed a

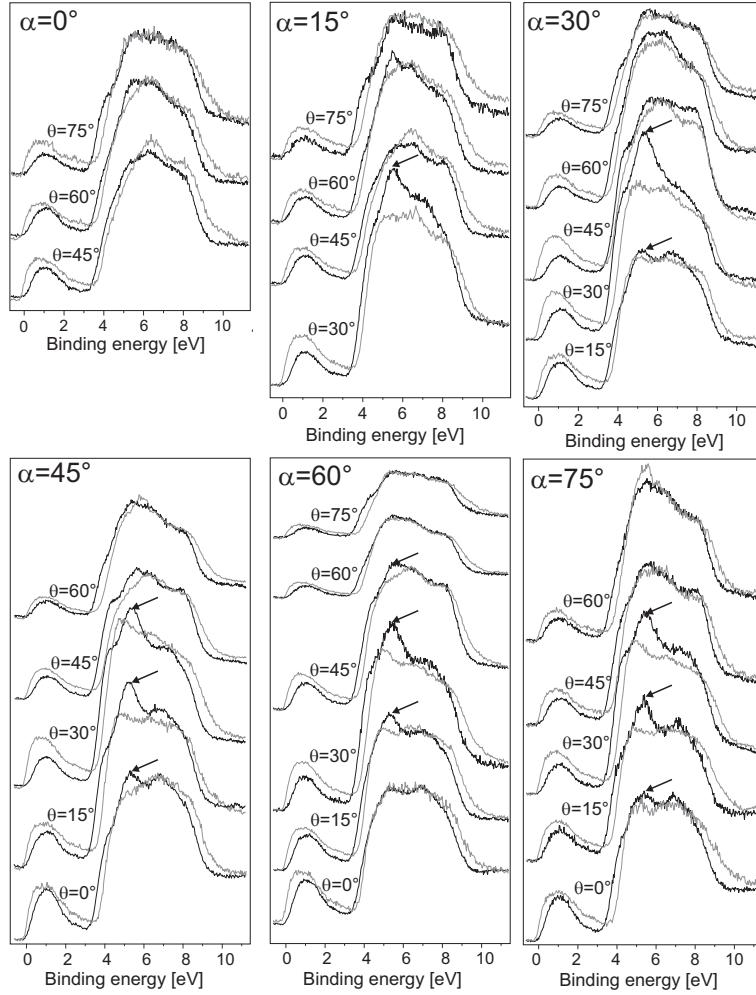


FIG. 3: ARUPS on $\text{V}_2\text{O}_3(0001)/\text{Au}(111)$ for the -V (grey) and -V=O (black) terminations - α is the light angle of incidence and θ the angle of detection

measurement series for 6 incidence angles and 6 detection angles ($0, 15^\circ, 30^\circ, 45^\circ, 60^\circ$ and 75°), the detector being positioned in the incidence plane. The results are shown in Figure 3.

For geometrical reasons only 28 different combinations of incident light and emission angles were available for measurement. The spectra were normalized to the background signal above E_F . No background has been removed.

As for the spectra of Figure 2, a shift of the O 2p band between both terminations is observed for each measurement geometry. A shift of the O 2p band away from E_F has been reported for Cr-doped V_2O_3 in [9] when the system becomes insulating. This shift is in the opposite direction than the one we observed. This suggests that there is no MIT in the bulk but that the effect observed concerns only the surface.

The spectra of the -V=O surface exhibit an additional spectral feature at about 5.5 eV, showing strong angular dependence. This feature is indicated on Figure 3 by

arrows. It is assigned to O 2p electrons of the vanadyl species.

For the -V=O termination, all spectra of Figure 3 exhibit a decrease of the emission intensity from the V 3d band and a narrowing of this band. More precisely, there is no spectral weight at the Fermi level, demonstrating the opening of a gap in the surface region. The opening of a similar gap was observed at the PM-AFI transition of pure V_2O_3 pure V_2O_3 [4, 10, 11, 12, 13] and of Cr-doped V_2O_3 single crystals [9]. We show for comparison in the inset of Figure 2 He I spectra in the V 3d region from [4] obtained on V_2O_3 single crystal above and below the transition temperature. Their spectra show a quite similar shape as ours. This gives evidence that the formation of vanadyl groups on the vanadium terminated surface therefore induces a MIT at the surface.

DISCUSSION

Formation of vanadyl groups on the V₂O₃ surface implies a change in the occupied states in the V 3d band. V 3d orbitals are supposed to mix with O 2p orbitals to form the double V-O bond of the vanadyl species. The V 3d band will then be partly depleted because V 3d electrons will be involved in the vanadyl bonding orbitals. In a metal, a simple decrease of the electronic density in the V 3d band should only lead to a "repositioning" of the Fermi level relative to the V 3d band. One would find a similar emission intensity at the Fermi level for both terminations. The difference for both terminations would simply be a narrowing of the V 3d band for the -V=O termination and a shift of the O 2p band relative to the Fermi level. Therefore, the decrease of emission at E_F for the -V=O surface evidences an opening of a gap. The band structure calculation performed by Mattheiss et al. [6] indicates that the partially filled bands at the Fermi surface of the metallic phase of bulk V₂O₃ involve all 5 a_{1g}, e_g^π and e_g^σ states. Thus, the gap we observed for the -V=O surface cannot result from a band effect but has to be interpreted as a correlation gap as it is the case for the low temperature phase of bulk V₂O₃.

The Mott transition can be characterized in photoemission by a decrease of emission at the Fermi level. In the framework of the so-called dynamical mean-field theory (DMFT), this change in emission from the d band is believed to correspond to a transfer of spectral weight from the region near the Fermi level to the upper and lower Hubbard bands. The DMFT has been used to explain photoemission spectra of 3d¹ compounds [14, 15, 16, 17]. These compounds show in the 3d emission region two features: the first one, just below E_F, is assigned to the coherent part of the single-particle spectral function, and the second one to its incoherent part (corresponding to the lower Hubbard band). The coherent part seems to correspond in this model to the density of states and is attributed to itinerant d-band states or quasi-particle excitations [15]. The changes in the emission from the V 3d band between both terminations reveal actually two effects: an opening of a correlation gap and a decrease of the electronic density in the V 3d band for the -V=O termination. Since the latter implies a decrease of the emission from the V 3d band, one may have some difficulty to interpret the former along the line of the DMFT, i.e. in terms of transfer of spectral weight.

The MIT we observed when vanadyl groups form on the surface is a very surprising effect. In a first approximation, formation of vanadyl groups can be interpreted as a doping of holes. It has been observed on ternary compounds [15] and also theoretically shown [18] that doping a Mott insulator with carriers (holes or electrons) leads to a transfer of spectral weight to the Fermi level. Formation of vanadyl groups should therefore favor the

metallic phase and not induce a MIT, as we experimentally observed. Theoretical treatments had therefore to be performed to understand the observed phenomenon properly.

In conclusion, we studied the electronic structure of thin films of V₂O₃(0001) with UV photoelectron spectroscopy (UPS). The results show a decrease of spectral weight at the Fermi level when vanadyl groups form on the vanadium terminated surface, evidencing a Mott transition.

ACKNOWLEDGMENT

We thank the Fritz-Haber-Institut for having supported this work and Silke Biermann for interesting discussions.

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